

MENU

SEARCH

INDEX

DETAIL

JAPANESE

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STATUS

1 / 1

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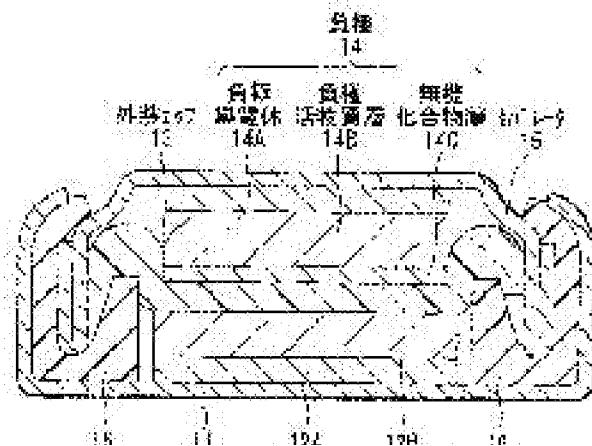
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(54) **NEGATIVE ELECTRODE AND BATTERY USING IT**

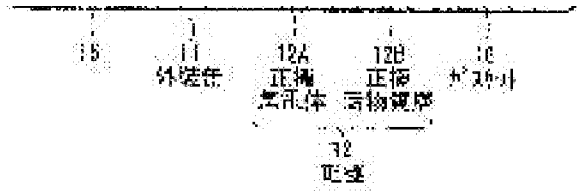
(57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative electrode having excellent cycle property, and a battery using the electrode.

SOLUTION: A positive electrode 12 and the negative electrode 14 are laid in layer via a separator 15 into which electrolyte is impregnated. The negative electrode 14 has a negative electrode collector 14A, a negative active material layer 14B and an inorganic compound layer 14C. The negative electrode active material layer 14B contains Si or its alloy and is formed by the gas phase method, liquid phase method or sintering method, and it is preferable that at least part of the interface with the negative electrode collector 14A is alloyed



with the negative electrode collector 14A. The inorganic compound layer 14C has lithium ion conductivity and is formed opposing to the positive electrode 12 of the negative electrode active material layer 14B. Because of the inorganic compound layer 14C, the reaction between the electrolyte and the negative electrode active material layer 14B is restrained and excellent cycle property can be provided.



JAPANESE

[JP,2004-171875,A]

Drawing selection

Representative draw

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS
DRAWINGS

[Translation done.]

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- 2.**** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

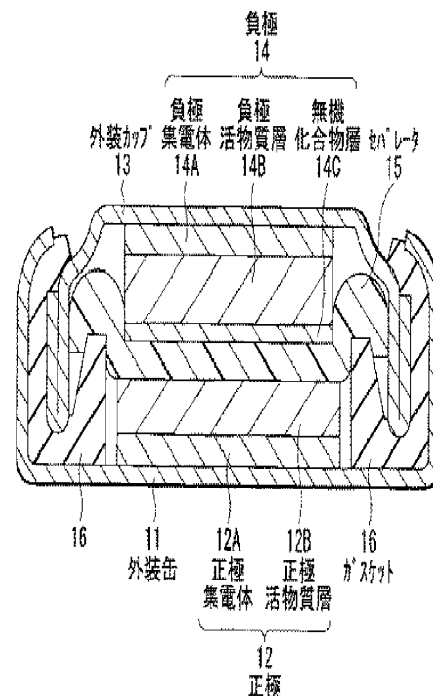
[Field of the Invention]

This invention relates to the negative electrode which has a negative pole collector and a negative electrode active material layer, and the cell using it.

[0002]

[Description of the Prior Art]

In recent years, it is anxious for high capacity-ization of the rechargeable battery which are those power supplies with highly-efficient-izing and multi-functionalization of mobile computing devices. There is a lithium secondary battery as a rechargeable battery which meets this demand. However, the cell capacity at the time of using cobalt acid lithium for an anode and using black lead for a negative electrode which is a typical gestalt of the lithium secondary battery in the present is in saturation, and large high capacity-ization is in a very difficult situation. Then, although using metal lithium (Li) for a negative electrode for many years is examined, in order to put this negative electrode in practical use, it is necessary to aim at



[Translation done.]

control of the improvement in the deposit dissolution efficiency of lithium, and a dendrite-like deposit gestalt, etc.

[0003]

On the other hand, examination of the negative electrode of high capacity using silicon (Si) or tin (Sn) is performed briskly these days. However, when these negative electrodes repeated charge and discharge, intense expansion and contraction of negative electrode active material ground, minuteness making was carried out, current collection nature fell, or it originated in increase of surface area, the decomposition reaction of the electrolysis solution was promoted, and the cycle characteristic was very inferior. Then, the negative electrode which formed the negative electrode active material layer in the negative pole collector with a gaseous phase method, a liquid phase process, or a sintering process is also examined (for example, refer to the patent documents 1, the patent documents 2, and patent documents 3.). According to this, compared with the conventional coating mold negative electrode which applied the slurry containing negative electrode active material, a binder, etc. of particle state, can control minuteness making, and. Since a negative pole collector and a negative electrode active material layer can be unified, the electron conductivity in a negative electrode becomes very good, and highly efficient-ization is expected also in cycle life also in capacity. Since a conducting material, a binder, an opening, etc. which existed in the negative electrode can also be reduced or eliminated conventionally, it becomes possible to thin-film-ize a negative electrode intrinsically.

[0004]

[Patent documents 1]

JP,8-50922,A

[Patent documents 2]

The patent No. 2948205 gazette

[Patent documents 3]

JP,11-135115,A

[0005]

[Problem(s) to be Solved by the Invention]

However, the negative electrode which formed the negative electrode active material layer in the negative pole collector with the gaseous phase method, the liquid phase process, or the sintering process was not able to be said to be it is difficult to avoid the decomposition reaction of the electrolysis solution in the surface of a negative electrode active material layer, and enough [a thing / a cycle characteristic], either.

[0006]

This invention was made in view of this problem, and the purpose is to provide the cell using the negative electrode and it which can acquire the outstanding cycle characteristic.

[0007]

[Means for Solving the Problem]

The 1st negative electrode of this invention is characterized by comprising:

Negative pole collector.

A negative electrode active material layer which it is provided in this negative pole collector, and an

interface with a negative pole collector sets in part at least, and is alloyed with a negative pole collector.
An inorganic compound layer which has the ion conductivity provided in this negative electrode active material layer.

[0008]

The 2nd negative electrode of this invention is characterized by comprising:

Negative pole collector.

A negative electrode active material layer formed by at least one method in a group which becomes this negative pole collector from a gaseous phase method, a liquid phase process, and a sintering process.

An inorganic compound layer which has the ion conductivity provided in this negative electrode active material layer.

[0009]

The 1st cell of this invention is characterized by comprising:

Having an electrolyte with an anode and a negative electrode, a negative electrode is a negative pole collector.

A negative electrode active material layer which it is provided in this negative pole collector, and an interface with a negative pole collector sets in part at least, and is alloyed with a negative pole collector.

An inorganic compound layer which has the ion conductivity provided in this negative electrode active material layer.

[0010]

The 2nd cell of this invention is characterized by comprising:

Having an electrolyte with an anode and a negative electrode, a negative electrode is a negative pole collector.

A negative electrode active material layer formed by at least one method in a group which becomes this negative pole collector from a gaseous phase method, a liquid phase process, and a sintering process.

An inorganic compound layer which has the ion conductivity provided in this negative electrode active material layer.

[0011]

In the 1st and 2nd negative electrodes by this invention, a reaction of a negative electrode active material layer and an electrolyte is inhibited by inorganic compound layer.

[0012]

In the 1st and 2nd cells by this invention, since a negative electrode of this invention is used, an outstanding cycle characteristic is acquired by inhibiting a reaction of a negative electrode active material layer and an electrolyte.

[0013]

[Embodiment of the Invention]

Hereafter, an embodiment of the invention is described in detail with reference to drawings.

[0014]

[A 1st embodiment]

Drawing 1 expresses the composition of the rechargeable battery concerning a 1st embodiment of this invention. This rechargeable battery is called what is called coin type, and the disc-like anode 12 accommodated in the armor can 11 and the disc-like negative electrode 14 accommodated in the exterior cup 13 are laminated via the separator 15. the gasket 16 of insulation [edge part / of the armor can 11 and the exterior cup 13] -- passing -- it is sealed by closing. The armor can 11 and the exterior cup 13 are constituted by metal, such as stainless steel or aluminum (aluminum), respectively, for example.

[0015]

The anode 12 is provided with the following.

For example, the positive pole collector 12A.

The positive active material layer 12B established in the positive pole collector 12A.

The positive pole collector 12A is constituted by aluminum, nickel (nickel), or stainless steel, for example.

[0016]

The positive active material layer 12B contains any one sort of occlusion and the positive electrode material which can be broken away, or two sorts or more for lithium as positive active material, and may contain binders, such as conducting materials, such as a carbon material, and polyvinylidene fluoride, if needed, for example. The lithium content metal multiple oxide expressed with general formula Li_xMIO_2 considering lithium as occlusion and a positive electrode material which can be broken away, for example is preferred. The lithium content metal multiple oxide can generate high tension, and it is because it is high-density, so further high capacity-ization of a rechargeable battery can be attained. MI is one or more kinds of transition metals, for example, either [at least] cobalt (Co) or the nickel is preferred. x changes with charge-and-discharge states of a cell, and is usually a value of $0.05 \leq x \leq 1.10$ within the limits. LiCoO_2 or LiNiO_2 is mentioned as an example of such a lithium content metal multiple oxide.

[0017]

The negative electrode 14 is provided with the following.

For example, the negative pole collector 14A.

The negative electrode active material layer 14B established in the negative pole collector 14A.

The inorganic compound layer 14C provided in the negative electrode active material layer 14B.

The negative pole collector 14A, the negative electrode active material layer 14B, and the inorganic compound layer 14C are laminated by this order, and they are arranged so that the inorganic compound layer 14C side may counter with the positive active material layer 12B of the anode 12.

[0018]

As for the negative pole collector 14A, it is preferred for there to be a certain amount of intensity and to be constituted with material with high conductivity, For example, it is preferred that at least one sort in the group which consists of copper (Cu), stainless steel, nickel, titanium (Ti), tungsten (W), molybdenum

(Mo), and aluminum is included. Especially, it may be more desirable for the metal which is easy to cause alloying with the negative electrode active material layer 14B to constitute. For example, when the negative electrode active material layer 14B contains at least one sort in the group which consists of the simple substance and compound of silicon or tin so that it may mention later, it is mentioned as a material which copper, titanium, aluminum, or nickel tends to alloy. Although a monolayer may constitute the negative pole collector 14A, two or more layers may constitute it. In that case, the negative electrode active material layer 14B and the metallic material which is easy to alloy constitute the layer which touches the negative electrode active material layer 14B, and it may be made for other metallic materials to constitute other layers.

[0019]

As for the surface roughness of the negative pole collector 14A, and arithmetic-mean-roughness Ra more specifically specified to JISB0601, it is preferred that it is 0.1 micrometers or more. By carrying out in this negative electrode 14, within the limits which mentioned surface roughness above, although the influence which expansion contraction of the negative electrode active material layer 14B accompanying charge and discharge has on the negative pole collector 14A is great, It is because the interface junction to the negative pole collector 14A and the negative electrode active material layer 14B can become powerful, it can control that the negative electrode active material layer 14B exfoliates from the negative pole collector 14A and a cycle characteristic can be raised as a result.

[0020]

The negative electrode active material layer 14B is formed by at least one method in the group which consists of a gaseous phase method, a liquid phase process, and a sintering process, for example, and is constituted including negative electrode active material. Thereby, destruction by expansion and contraction of the negative electrode active material layer 14B accompanying charge and discharge can be controlled, and the negative pole collector 14A and the negative electrode active material layer 14B can be unified, and the electron conductivity in the negative electrode 14 can be raised now. It is also possible to differ from the conventional coating mold negative electrode, to be able to reduce or eliminate a binder, an opening, etc., and to thin-film-ize. As for this negative electrode active material layer 14B, it is preferred for an interface with the negative pole collector 14A to set in part at least, and to alloy with the negative pole collector 14A. Specifically, it is preferred that the negative pole collector 14A or they are mutually spread [the composing element of the negative pole collector 14A] by the composing element of the negative electrode active material layer 14B or negative electrode active material in an interface. When this alloying forms the negative electrode active material layer 14B with a gaseous phase method, a liquid phase process, or a sintering process, it takes place simultaneously in many cases, but what happened by performing heat treatment may be used for it. In this specification, diffusion of the element mentioned above is also included in one gestalt of alloying.

[0021]

It is preferred that at least one sort in the group which consists of the simple substance and compound of silicon or tin is included as negative electrode active material. It is because the simple substance and compound of silicon or tin can form lithium etc. and an alloy, and occlusion and their capability from

which it secedes are large in lithium and the energy density of the negative electrode 14 can be made high as compared with conventional black lead depending on combination. As a compound of silicon or tin, for example, SiB_4 , SiB_6 , Mg_2Si , Mg_2Sn , nickel_2Si , TiSi_2 , MoSi_2 , CoSi_2 , NiSi_2 , CaSi_2 , CrSi_2 , Cu_5Si , FeSi_2 , MnSi_2 , NbSi_2 , TaSi_2 , VSi_2 , WSi_2 , ZnSi_2 , SiC , Si_3N_4 , $\text{Si}_2\text{N}_2\text{O}$, SiO_v ($0 < v \leq 2$), SnO_w ($0 < w \leq 2$), SnSiO_3 , LiSiO , or LiSnO is mentioned.

[0022]

The inorganic compound layer 14C is for inhibiting the reaction of the electrolysis solution and the negative electrode active material layer 14B which are mentioned later, and has lithium ion conductivity. It is preferred that 10 nm is less than [super-5micrometer], and if the thickness of the inorganic compound layer 14C is not less than 50 nm 3 micrometers or less, it is more preferred. When too thin, it is difficult to fully inhibit the reaction of an electrolysis solution and the negative electrode active material layer 14B, and it is because there is a possibility of breakage etc. breaking out, resistance increasing if too conversely thick, and reducing the load characteristic of the whole cell greatly by expansion and contraction of the negative electrode active material layer 14B by charge and discharge.

[0023]

As a component of the inorganic compound layer 14C, reduction tolerance and reactivity with lithium, From viewpoints of pliability, intensity, or ionic conductivity to lithium fluoride (LiF). A lithium bromide (LiBr), lithium iodide (LiI), a lithium chloride (LiCl), Lithium nitride (Li_3N), a lithium sulfide (Li_2S), A lithium silicate (Li_4SiO_4), lithium carbonate (Li_2CO_3), The thing containing at least one sort of lithium compounds of the groups which consist of a nitride (LiPON) of lithium sulfate (Li_2SO_4), Lynn-ized lithium (Li_3P), lithium phosphate (Li_3PO_4), and lithium phosphate is preferred. Especially, especially the thing containing the nitride of lithium phosphate is preferred from points, such as pliability, intensity or ionic conductivity. The chemical formula shown in the parenthesis here may be stoichiometric composition, and the above-mentioned lithium compound may not be stoichiometric composition.

[0024]

What was produced as a component of the inorganic compound layer 14C using at least one sort in the lithium compound mentioned above to raw material is preferred. As such a lithium compound, lithium phosphate is used as raw material and there is a nitride of the lithium phosphate obtained by performing reactive sputtering into a nitrogen gas atmosphere, for example.

[0025]

In order to raise ion conductivity as a component of the inorganic compound layer 14C to the thing containing the above-mentioned lithium compound, what added other compounds, such as aluminum, a silica dioxide (SiO_2), or a phosphorus sulfide (P_2S_5), may be used. As a thing containing other compounds, the solid solution ($\text{Li}_2\text{S}-\text{P}_2\text{S}_5$) of a lithium sulfide and a phosphorus sulfide or the solid solution ($\text{Li}_2\text{S}-\text{SiS}_2$) of a lithium sulfide and a silicon sulfide is mentioned. The chemical formula shown

in the parenthesis also here may be stoichiometric composition, and the above-mentioned lithium compound may not be stoichiometric composition.

[0026]

It may have crystallinity, although the amorphous thing of the component of these inorganic compound layers 14C is preferred.

[0027]

Here, the capacity in the actual use charge-and-discharge-voltage field of the negative electrode 14 is expressed by the occlusion of lithium, and the capacity component by secession.

[0028]

It passes a lithium ion, the separator 15 isolating the anode 12 and the negative electrode 14, and preventing the short circuit of the current by contact of two poles. This separator 15 is constituted by polyethylene and polypropylene, for example.

[0029]

The electrolysis solution which is a liquefied electrolyte is impregnated with the separator 15. This electrolysis solution contains a solvent and lithium salt which is the electrolyte salt dissolved in this solvent, for example, and may contain the additive agent if needed. Thus, if an electrolysis solution is used, since high ionic conductivity can be obtained, it is desirable. As a solvent, organic solvents, such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, or ethyl methyl carbonate, are mentioned, and any these one sort or two sorts or more may be mixed and used, for example.

[0030]

As lithium salt, LiPF_6 or LiClO_4 may be mentioned, these may be used independently, for example, and it may mix and use.

[0031]

This rechargeable battery can be manufactured as follows, for example.

[0032]

First, for example, after mixing positive active material, a conducting material, and a binder and adjusting positive electrode mixture, carrier fluid, such as N-methyl pyrrolidone, is made to distribute this positive electrode mixture, and it is considered as a positive electrode mixture slurry. Then, after applying this positive electrode mixture slurry to the positive pole collector 12A and making it dry, compression molding is carried out, the positive active material layer 12B is formed, and the anode 12 is produced.

[0033]

Subsequently, the negative electrode active material layer 14B is formed by making the negative pole collector 14A deposit at least one sort in the group which consists of the simple substance and compound of negative electrode active material, for example, silicon, or tin with a gaseous phase method or a liquid phase process. After forming in the negative pole collector 14A the precursive layer containing the negative electrode active material of particle state, The negative electrode active material layer 14B may be formed with the sintering process which makes this sinter, and it may be made to form the negative

electrode active material layer 14B combining two or three methods in a gaseous phase method, a liquid phase process, and a sintering process. Thus, by forming the negative electrode active material layer 14B by at least one method in the group which consists of a gaseous phase method, a liquid phase process, and a sintering process, depending on the case, an interface with the negative pole collector 14A sets in part at least, and the negative pole collector 14A and the alloyed negative electrode active material layer 14B are formed. In order to make the interface of the negative pole collector 14A and the negative electrode active material layer 14B alloy more, it may be made to heat-treat under a vacuum atmosphere or a non-oxidizing atmosphere. When forming by plating which mentions the negative electrode active material layer 14B later especially, since it may be hard to alloy the negative electrode active material layer 14B also in an interface with the negative pole collector 14A, it is preferred to perform this heat treatment if needed. Since the characteristic may be raised by making the interface of the negative pole collector 14A and the negative electrode active material layer 14B alloy more when forming by a gaseous phase method, it is preferred to perform this heat treatment if needed.

[0034]

As a gaseous phase method, according to the kind of negative electrode active material, can use the physical depositing method or chemical deposition method, and specifically, a vacuum deposition method, a sputtering technique, the ion plating method, a laser ablation method, and the heat CVD (Chemical Vapor Deposition; chemical vapor deposition) -- low or plasma CVD method is available. As a liquid phase process, publicly known techniques, such as electrolysis plating or electroless plating, are available. A publicly known technique is available also about a sintering process, for example, an atmosphere sintering process, a reaction sintering method, or a hotpress sintering process is available.

[0035]

After forming the negative electrode active material layer 14B, by sputtering techniques, such as vacuum deposition or a reactive sputtering method, the inorganic compound layer 14C is formed in the negative electrode active material layer 14B, and the negative electrode 14 is produced.

[0036]

The separator 15 and the anode 12 which were impregnated with the negative electrode 14 and the electrolysis solution after it are laminated, it puts in the exterior cup 13 and the armor can 11, and they are closed. Thereby, the rechargeable battery shown in drawing 1 is obtained.

[0037]

The inorganic compound layer 14C adds the precursor of the component of the inorganic compound layer 14C, and it may be made to form it into an electrolysis solution by making it deposit on the negative electrode active material layer 14B. The deposit may be performed at the time of an assembly of a rechargeable battery, and charge may perform after an assembly.

[0038]

This rechargeable battery acts as follows.

[0039]

In this rechargeable battery, if it charges, a lithium ion will secede from the anode 12 and occlusion will be carried out to the negative electrode 14 via an electrolysis solution. If it discharges, a lithium ion will

secede from the negative electrode 14, and occlusion will be carried out to the anode 12 via an electrolysis solution, for example. In that case, the reaction of an electrolysis solution and the negative electrode active material layer 14B is inhibited by the inorganic compound layer 14C.

[0040]

Thus, according to this embodiment, since the inorganic compound layer 14C was formed in the anode 12 of the negative electrode active material layer 14B, and the side which counters, the reaction of an electrolysis solution and the negative electrode active material layer 14B can be inhibited, and, thereby, the outstanding cycle characteristic can be acquired, for example.

[0041]

Especially to the inorganic compound layer 14C. If it is made for at least one sort in the group which consists of a nitride of lithium fluoride, a lithium bromide, lithium iodide, a lithium chloride, lithium nitride, a lithium sulfide, a lithium silicate, lithium carbonate, lithium sulfate, Linn-ized lithium, lithium phosphate, and lithium phosphate to be included, Pliability, intensity, or ionic conductivity of the inorganic compound layer 14C, etc. can be raised. Especially, a higher effect can be acquired if it is made for the nitride of lithium phosphate to be included.

[0042]

If 10 nm of thickness of the inorganic compound layer 14C is made into less than [super-5micrometer], the reaction of an electrolysis solution and the negative electrode active material layer 14B can be inhibited more, and a higher effect can be acquired.

[0043]

In this embodiment, since the electrolysis solution was used as an electrolyte, high ionic conductivity can be obtained.

[0044]

[A 2nd embodiment]

Drawing 2 decomposes and expresses the composition of the rechargeable battery concerning a 2nd embodiment of this invention. This rechargeable battery accommodates the electrode winding body 30 to which the positive electrode lead 21 and the negative electrode lead 22 were attached in the inside of the exterior members 40A and 40B of film state, and a miniaturization, a weight saving, and slimming down are possible for it.

[0045]

The positive electrode lead 21 and the negative electrode lead 22 are drawn from the inside of the exterior members 40A and 40B by the uniform direction toward the exterior, respectively. The positive electrode lead 21 and the negative electrode lead 22 are constituted by metallic materials, such as aluminum, copper, nickel, or stainless steel, respectively, and are made into thin plate state or mesh shape, respectively, for example.

[0046]

The exterior members 40A and 40B are constituted by the aluminum laminate film of the rectangular shape which pasted together a nylon film, aluminium foil, and a polyethylene film to this order, for example. The exterior members 40A and 40B are allocated, for example so that the electrode winding

body 30 may counter the polyethylene film side, and they are mutually stuck to each outer edge section by weld or adhesives. Between the exterior members 40A and 40B, the positive electrode lead 21, and the negative electrode lead 22, the adhesion film 41 for preventing invasion of the open air is inserted. The adhesion film 41 is constituted by polyolefin resin, such as the material which has adhesion to the positive electrode lead 21 and the negative electrode lead 22, for example, polyethylene, polypropylene, modified polyethylene, or denaturation polypropylene.

[0047]

The exterior members 40A and 40B are replaced with the aluminum laminate film mentioned above, and it may be made for the high polymer film or metallic films which have other structures, such as a laminate film and polypropylene, to constitute them.

[0048]

Drawing 3 expresses the section structure which met the III-III line of the electrode winding body 30 shown in drawing 2. The electrode winding body 30 laminates and winds the band-like anode 31 and the negative electrode 32 via the separator 33 and the electrolyte layer 34, and the outermost periphery part is protected by the masking tape 35.

[0049]

The anode 31 has the structure where the positive active material layer 31B was established in one side or both sides of the positive pole collector 31A, and the negative electrode 32 has the structure where the negative electrode active material layer 32B was established in one side or both sides of the negative pole collector 32A. The inorganic compound layer 32C is formed in the negative electrode active material layer 32B. The composition of the positive pole collector 31A, the positive active material layer 31B, the negative pole collector 32A, the negative electrode active material layer 32B, the inorganic compound layer 32C, and the separator 33 is the same as that of a 1st embodiment.

[0050]

The electrolyte layer 34 is constituted by what is called gel electrolyte that made the electrolysis solution hold to a supporter. High ionic conductivity is obtained with an electrolysis solution, and since the gel electrolyte can prevent bulging a liquid spill of a cell or hot by a supporter, it is preferred. The composition of an electrolysis solution (namely, a solvent and electrolyte salt) is the same as that of a 1st embodiment.

[0051]

The supporter is constituted by the polymer material, for example. As a polymer material, the polyvinylidene fluoride which is a block copolymer, for example is mentioned.

[0052]

This rechargeable battery can be manufactured as follows, for example.

[0053]

First, like a 1st embodiment, after producing the anode 31 and the negative electrode 32, the electrolyte layer 34 where the electrolysis solution was held at the supporter is formed in each of the anode 31 and the negative electrode 32. After it, the positive electrode lead 21 is attached to the end of the positive pole collector 31A by welding, and the negative electrode lead 22 is attached to the end of the negative pole

collector 32A by welding.

[0054]

Subsequently, after laminating the anode 31 and the negative electrode 32 in which the electrolyte layer 34 was formed via the separator 33 and considering it as a layered product, this layered product is wound around that longitudinal direction, the masking tape 35 is pasted up on an outermost periphery part, and the electrode winding body 30 is formed.

[0055]

Finally, the electrode winding body 30 is put among the exterior members 40A and 40B, the outer edge sections of the exterior members 40A and 40B are stuck by thermal melting arrival etc., and they are enclosed, for example. In that case, the adhesion film 41 is inserted between the positive electrode lead 21 and the negative electrode lead 22, and the exterior members 40A and 40B. Thereby, the rechargeable battery shown in drawing 2 and drawing 3 is completed.

[0056]

This rechargeable battery can act like a 1st embodiment, and can acquire the same effect. In particular, in this rechargeable battery, since the gel electrolyte was used as an electrolyte, high ionic conductivity can be obtained, and bulging a liquid spill of a cell or hot can be prevented.

[0057]

[Example]

The concrete example of this invention is described in detail.

[0058]

(Example 1-1 to 1-5)

The coin type cell which has the shape shown in drawing 1 was produced. Therefore, here explains with reference to drawing 1 using the numerals. Here, the metal lithium board was used as a counter electrode of the negative electrode 14.

[0059]

First, arithmetic-mean-roughness Ra formed the negative electrode active material layer 14B with a thickness of 3 micrometers which consists of silicon with an electron beam vacuum deposition method on the negative pole collector 14A with a thickness of 20 micrometers which consists of electrolytic copper foil which is 1.5 micrometers. The inorganic compound layer 14C which consists of lithium phosphate (Li_3PO_4) with a resistance heating vacuum deposition method was formed after it and on the negative electrode active material layer 14B, and the negative electrode 14 was produced. In that case, the thickness of the inorganic compound layer 14C was changed, as Example 1-1 to 1-5 showed to Table 1. The place which analyzed the obtained negative electrode 14 by XPS (X-ray Photoelectron Spectroscopy; X-ray photoelectron spectroscopy) and AES (Auger Electron Spectroscopy; Auger electron spectroscopy), It was checked that an interface with the negative pole collector 14A sets in part at least, and the negative electrode active material layer 14B is alloying with the negative pole collector 14A.

[0060]

Subsequently, laminate the negative electrode 14 and the 25-micrometer-thick separator 15 made from

polypropylene in the center section of the exterior cup 13 one by one, and an electrolysis solution is injected into it. As a counter electrode of the negative electrode 14, the armor can 11 into which the 1-mm-thick metal lithium board was put was put, and a coin type cell a caulking, 20 mm in diameter, and 1.6 mm in height was produced. What dissolved LiPF_6 which is lithium salt in the solvent which mixed

ethylene carbonate 40 mass % and diethyl carbonate 60 mass % so that it might become 1.0 mol/dm^3 was used for the electrolysis solution.

[0061]

[Table 1]

| | 負極集電体の 算術平均粗さ Ra (μm) | 負極 活物質層 | 無機化合物層 | | 10 サイクル後 容量維持率 (%) |
|---------|---|------------|--------------------------|---------|--------------------------|
| | | | 構成材料 | 厚み (nm) | |
| 実施例 1-1 | 1.5 | Si 蒸着 | Li_3PO_4 | 10 | 71 |
| 実施例 1-2 | 1.5 | Si 蒸着 | Li_3PO_4 | 50 | 81 |
| 実施例 1-3 | 1.5 | Si 蒸着 | Li_3PO_4 | 500 | 92 |
| 実施例 1-4 | 1.5 | Si 蒸着 | Li_3PO_4 | 3000 | 83 |
| 実施例 1-5 | 1.5 | Si 蒸着 | Li_3PO_4 | 5000 | 72 |
| 比較例 1 | 1.5 | Si 蒸着 | — | 0 | 70 |

[0062]

About the coin type cell of acquired Example 1-1 to 1-5, the charge and discharge test was done and the 10 cycles after capacity maintenance rate was searched for. Charge was the constant current density of 1 mA/cm^2 at that time, and after carrying out until cell voltage amounted to 0V, it carried out until current density declined to 0.01 mA/cm^2 with the constant voltage of 0V, and discharge was performed until cell

voltage amounted to 2.0V by the constant current density of 1 mA/cm². The 10 cycles after capacity maintenance rate was computed as the ratio of the service capacity of 10 cycle eye to first time service capacity, i.e., (10 service capacity of a cycle eye) / (first time service capacity) x100. The obtained result is shown in Table 1.

[0063]

As the comparative example 1 over Example 1-1 to 1-5, others produced the coin type cell like Example 1-1 to 1-5 except for not forming an inorganic compound layer. Also about the coin type cell of the comparative example 1, like Example 1-1 to 1-5, the charge and discharge test was done and the 10 cycles after capacity maintenance rate was searched for. The result is also shown according to Table 1.

[0064]

As shown in Table 1, the high capacity maintenance rate was acquired compared with the comparative example 1 which did not form Example 1-1 to 1-5 in which the inorganic compound layer 14C was formed. Although the effect was large, the thickness of the inorganic compound layer 14C receives in Example 1-2 to 1-4 of less than 5000 10-nm super-nm (5 micrometers), so that Example 1-1 to 1-5 may show, In Example 1-1 whose thickness of the inorganic compound layer 14C is 10 nm, and Example 1-5 whose thickness of the inorganic compound layer 14C is 5 micrometers, the effect was small. This is too thin to fully inhibit the reaction of the negative electrode active material layer 14B and an electrolysis solution at 10 nm or less, Since resistance of the negative electrode 14 increased and capacity fell with the decomposition product of the generated electrolysis solution, it thinks, and by not less than 5 micrometers, resistance of the inorganic solid electrolyte layer 14C itself increases, and it thinks because resistance of the cell went up greatly and capacity was not able to be taken out.

[0065]

That is, it turned out that a cycle characteristic can be raised if the inorganic compound layer 14C is formed in the negative electrode active material layer 14B, and a higher effect can be acquired if 10 nm of the thickness shall be less than [super-5micrometer] and also not less than 50 nm 3 micrometers or less.

[0066]

(Example 2-1 to 2-4)

Except for having used the negative pole collector 14A with a thickness of 20 micrometers which has arithmetic-mean-roughness Ra shown in Table 2, others produced the coin type cell like Example 1-3. Also about the coin type cell of Example 2-1 to 2-4, the charge and discharge test was done like Example 1-1 to 1-5, and the 10 cycles after capacity maintenance rate was searched for. The result is shown in Table 2 with the result of Example 1-3 and the comparative example 1. When XPS and AES analyzed the negative electrode 14 of Example 2 as well as Example 1-1 to 1-5, it was checked that an interface with the negative pole collector 14A sets in part at least, and the negative electrode active material layer 14B is alloying with the negative pole collector 14A.

[0067]

[Table 2]

| | 負極集電体の 算術平均粗さ Ra (μm) | 負極 活性物質層 | 無機化合物層 | | 10 サイクル後 容量維持率 (%) |
|---------|---|-------------|--------------------------|---------|--------------------------|
| | | | 構成材料 | 厚み (nm) | |
| 実施例 2-1 | 0.05 | Si 蒸着 | Li_3PO_4 | 500 | 80 |
| 実施例 2-2 | 0.1 | Si 蒸着 | Li_3PO_4 | 500 | 88 |
| 実施例 2-3 | 0.5 | Si 蒸着 | Li_3PO_4 | 500 | 90 |
| 実施例 1-3 | 1.5 | Si 蒸着 | Li_3PO_4 | 500 | 92 |
| 実施例 2-4 | 2.5 | Si 蒸着 | Li_3PO_4 | 500 | 91 |
| 比較例 1 | 1.5 | Si 蒸着 | — | 0 | 70 |

[0068]

As shown in Table 2, in the capacity maintenance rate, arithmetic-mean-roughness Ra of of 0.1 micrometers or more Example 2-2 - 2-4, 1-3 of the negative pole collector 14A was improving greatly compared with not less than 88% and 80% of Example 2-1 whose arithmetic-mean-roughness Ra is 0.05 micrometer. That is, when arithmetic-mean-roughness Ra used the negative pole collector 14A of 0.1 micrometers or more, it turned out that a cycle characteristic can be raised greatly.

[0069]

(Example 3-1 to 3-5)

After forming the negative electrode active material layer 14B with a thickness of 3 micrometers which becomes the same negative pole collector 14A as Example 1-1 to 1-5 from tin by plating, in the vacuum, this was heat-treated at 200 °C for 10 hours. The inorganic compound layer 14C which consists of lithium fluoride (LiF) with a resistance heating vacuum deposition method was formed in the negative electrode active material layer 14B after it, and the negative electrode 14 was produced. In that case, the thickness of the inorganic compound layer 14C was changed, as Example 3-1 to 3-5 showed to Table 3. When XPS

and AES analyzed the negative electrode 14 of Example 3-1 to 3-5 as well as Example 1-1 to 1-5, it was checked that an interface with the negative pole collector 14A sets in part at least, and the negative electrode active material layer 14B is alloying with the negative pole collector 14A. Except for having used this negative electrode 14, others produced the coin type cell like Example 1-1 to 1-5. Except for not forming an inorganic compound layer, others produced the coin type cell like Example 3-1 to 3-5 as the comparative example 3 over Example 3-1 to 3-5. Also about the coin type cell of Example 3-1 to 3-5, and the comparative example 3, the charge and discharge test was done like Example 1-1 to 1-5, and the 10 cycles after capacity maintenance rate was searched for. The result is shown in Table 3.

[0070]

[Table 3]

| | 負極集電体の 算術平均粗さ Ra (μm) | 負極 活物質層 | 無機化合物層 | | 10 サイクル後 容量維持率 (%) |
|---------|---|------------|--------|---------|--------------------------|
| | | | 構成材料 | 厚み (nm) | |
| 実施例 3-1 | 1.5 | Sn 鍍金 | LiF | 10 | 73 |
| 実施例 3-2 | 1.5 | Sn 鍍金 | LiF | 50 | 80 |
| 実施例 3-3 | 1.5 | Sn 鍍金 | LiF | 500 | 86 |
| 実施例 3-4 | 1.5 | Sn 鍍金 | LiF | 3000 | 77 |
| 実施例 3-5 | 1.5 | Sn 鍍金 | LiF | 5000 | 73 |
| 比較例 3 | 1.5 | Sn 鍍金 | — | 0 | 71 |

[0071]

As shown in Table 3, also in Example 3-1 to 3-5, the same tendency as Example 1-1 to 1-5 was seen. Namely, if it is not based on the component of the inorganic compound layer 14C but the inorganic compound layer 14C is formed in the negative electrode active material layer 14B, When the cycle

characteristic could be raised and 10 nm of the thickness was less than [super-5micrometer] and also not less than 50 nm 3 micrometers or less, it turned out that a higher effect can be acquired.

[0072]

(Example 4)

The rechargeable battery which has the shape shown in drawing 2 and drawing 3 was produced using the gel electrolyte. Therefore, here explains with reference to drawing 2 and drawing 3 using the numerals.

[0073]

First, the powder of cobalt acid lithium (LiCoO_2) with a mean particle diameter of 5 micrometers which is positive active material, Carbon black which is a conducting material, and the polyvinylidene fluoride which is binders, cobalt-acid-lithium: -- carbon black: -- with the mass ratio of polyvinylidene fluoride =92:3:5, [mix and] This was supplied to N-methyl pyrrolidone which is carrier fluid, and it was considered as the positive electrode mixture slurry, it applies to the positive pole collector 31A which consists of 30-micrometer-thick aluminum, and it was dried, by pressurizing, the positive active material layer 31B was formed, and the anode 31 was produced.

[0074]

With a mean particle diameter of 1 micrometer which is negative electrode active material on negative pole collector 32A with a thickness of 20 micrometers which arithmetic-mean-roughness Ra becomes from electrolytic copper foil which is 1.5 micrometers silicon powder 90 mass %, Mix polyvinylidene fluoride 10 mass % which is a binder, supply this to N-methyl pyrrolidone which is carrier fluid, and it is considered as a negative electrode mixture slurry, After applying this to the negative pole collector 32A, making it dry and pressurizing, it sintered by performing heat treatment at 350 ** under a vacuum atmosphere for 12 hours, and the negative electrode active material layer 32B was formed. By RF sputtering technique using lithium phosphate as a target after it, using the mixed gas of argon (Ar) and nitrogen (N_2) as discharge gas. On the negative electrode active material layer 32B, the inorganic compound layer 32C containing the nitride (LiPON) of lithium phosphate and lithium phosphate was formed by a thickness of 500 nm, and the negative electrode 32 was produced.

[0075]

Ethylene carbonate 42.5 mass % after producing the anode 31 and the negative electrode 32, Polyvinylidene fluoride 10 mass % which is the block copolymerization of the weight average molecular weight 600,000 at electrolysis solution 30 mass % which consists of propylene carbonate 42.5 mass % and LiPF_6 15 mass % which is lithium salt, By applying to each of the anode 31 and the negative electrode 32 the precursor solution which mixed dimethyl carbonate 60 mass % which is a solvent of a polymer material and in which it was made to dissolve, neglecting it at ordinary temperature for 8 hours, and volatilizing dimethyl carbonate, The electrolyte layer 34 was formed on each of the anode 31 and the negative electrode 32.

[0076]

Subsequently, cut the anode 31 and the negative electrode 32 to band-like, and the positive electrode lead

21 was attached to the anode 31, and the negative electrode lead 22 was attached to the negative electrode 32. After it, the anode 31 and the negative electrode 32 in which the electrolyte layer 34 was formed were laminated, it was considered as the layered product, and the electrode winding body 30 was formed by winding this layered product.

[0077]

It sealed by pinching this electrode winding body 30 among the exterior members 40A and 40B which consist of aluminum laminate films, and carrying out thermal melting arrival to the last under decompression. The adhesion film 41 which consists of resin was inserted between the positive electrode lead 21 and the negative electrode lead 22, and the exterior members 40A and 40B at that time. By the above, the rechargeable battery shown in drawing 2 and drawing 3 was obtained.

[0078]

About the rechargeable battery of acquired Example 4, the charge and discharge test was done and the 30 cycles after capacity maintenance rate was searched for. After carrying out until charge is the constant current density of 2 mA/cm² and cell voltage amounts to 4.2V in that case, It carried out until current density declined to 0.02 mA/cm² with the constant voltage of 4.2V, and discharge was performed until cell voltage amounted to 2.5V by the constant current density of 2 mA/cm². When charging, based on the charge-and-discharge capacity of the anode 31 and the negative electrode 32 for which it asked by calculation beforehand, the negative-electrode capacity factor in first-time charge is set to 90%, and metal lithium was kept from depositing. The 30 cycles after capacity maintenance rate was computed as the ratio of the service capacity of 30 cycle eye to first time service capacity, i.e., (30 service capacity of a cycle eye) / (first time service capacity) x100. The obtained result is shown in Table 4.

[0079]

[Table 4]

| | 負極 活物質層 | 無機化合物層 | | 30 サイクル後 容量維持率 (%) |
|---------|------------|---|---------|--------------------------|
| | | 構成材料 | 厚み (nm) | |
| 実施例 4 | Si 焼結 | $\text{Li}_3\text{PO}_4 + \text{LiPON}$ | 500 | 92 |
| 比較例 4-1 | Si 焼結 | — | 0 | 81 |
| 比較例 4-2 | Si 塗布 | $\text{Li}_3\text{PO}_4 + \text{LiPON}$ | 500 | 21 |
| 比較例 4-3 | Si 塗布 | — | 0 | 33 |

[0080]

As the comparative example 4-1 over Example 4, others produced the rechargeable battery like Example 4 except for not forming an inorganic compound layer. It formed by applying a negative electrode active material layer as comparative example 4-2,4-3 to Example 4, and others produced the rechargeable battery like Example 4 except for having changed the thickness of the inorganic compound layer, as shown in Table 4. Silicon powder 70 mass part with a mean particle diameter of 1 micrometer whose negative electrode active material layer is negative electrode active material in that case, Graphitization vapor-phase-epitaxy carbon fiber 5 mass part and scale-like artificial-graphite 20 mass part which are negative electrode active material and a conducting material, and polyvinylidene fluoride 10 mass part which is binders were mixed, and it formed by applying this to the same negative pole collector as Example 1-1 to 1-5, making it dry, and pressurizing. Also about the rechargeable battery of the comparative example 4-1 to 4-3, the charge and discharge test was done like Example 4, and the 30 cycles after capacity maintenance rate was searched for. The result is also shown according to Table 4. When XPS and AES analyzed the negative electrode 22 of Example 4 as well as Example 1-1 to 1-15, it was checked that an interface with the negative pole collector 32A sets in part at least, and the negative electrode active material layer 32B is alloying with the negative pole collector 32A.

[0081]

As shown in Table 4, the high capacity maintenance rate was acquired compared with the comparative example 4-1 which the direction of Example 4 in which the inorganic compound layer 32C was formed

did not form. On the other hand, in comparative example 4-2,4-3 which formed the negative electrode active material layer by spreading, the 30 cycles after capacity maintenance rate in which the comparative example 4-3 which did not form an inorganic compound layer is higher than the formed comparative example 4-2 was acquired. As for this, a negative pole collector and a negative electrode active material layer do not alloy the negative electrode of comparative example 4-2,4-3. The structural failure of a negative electrode active material layer happens by expansion and contraction of the negative electrode active material layer accompanying charge and discharge. It not only loses the capability to control disassembly of the electrolysis solution which an inorganic compound layer originally has, but the inorganic compound layer which this formed in the surface exfoliates, and it thinks because the inorganic compound layer has had the adverse effect as an insulator in a negative electrode active material layer. That is, in the rechargeable battery which has the negative electrode active material layer 32B which the interface of the negative pole collector 32A set in part at least with the sintering process, and was made to alloy with the negative pole collector 32A, when forming the inorganic compound layer 32C, it turned out that a cycle characteristic can be raised.

[0082]

Although the above-mentioned example gave and explained the example about the component of the inorganic compound layers 14C and 32C, the same result can be obtained even if it forms the inorganic compound layers 14C and 32C with other materials which have ion conductivity.

[0083]

As mentioned above, although the embodiment and the example were given and this invention was explained, this invention is not limited to the above-mentioned embodiment and an example, and is variously deformable. For example, although the above-mentioned embodiment and the example explained the case where the electrolysis solution which is a liquefied electrolyte, or what is called a gel electrolyte was used, it may be made to use other electrolytes. The thing which mixed the solid electrolyte which has ion conductivity, the solid electrolyte, and the electrolysis solution as other electrolytes, or the thing which mixed the solid electrolyte and the gel electrolyte is mentioned.

[0084]

The inorganic solid electrolyte which consists of the solid polymer electrolyte which, for example, made the high molecular compound which has ion conductivity distribute electrolyte salt, ion conducting glass, or an ionicity crystal can be used for a solid electrolyte. Ether system high molecular compounds, such as a bridging body which contains polyethylene oxide or polyethylene oxide as a high molecular compound, for example at this time, ester system high molecular compounds, such as polymethacrylate, and an acrylate system high molecular compound, or into a molecule, it can mix, or copolymerization can be carried out and it can use. Lithium nitride or lithium phosphate can be used as an inorganic solid electrolyte.

[0085]

In the above-mentioned embodiment and the example, although the inorganic compound layers 14C and 32C were formed in the negative electrode active material layers 14B and 32B, the inorganic compound layer should just be located in the anode side of a negative electrode active material layer, for example,

other layers may be inserted between the negative electrode active material layer and the inorganic compound layer.

[0086]

Although the negative electrode active material layers 14B and 32B were formed in the negative pole collectors 14A and 32A, it may be made to form other layers between a negative pole collector and a negative electrode active material layer in the above-mentioned embodiment and an example.

[0087]

In addition, in the above-mentioned embodiment and an example, although the coin type or the winding lamination type rechargeable battery was explained, this invention is applicable to a cylindrical, square shape, button type, thin shape, large size, and lamination lamination type rechargeable battery similarly. It is applicable not only to a rechargeable battery but a primary battery.

[0088]

[Effect of the Invention]

As explained above, the negative electrode according to any one of claims 1 to 8, Or since the inorganic compound layer was provided in the negative electrode active material layer according to the cell according to any one of claims 9 to 19, the reaction of an electrolyte and a negative electrode active material layer can be inhibited, and, thereby, the outstanding cycle characteristic can be acquired.

[0089]

According to the negative electrode according to claim 5 or the cell according to claim 13, especially. To an inorganic compound layer. At least one sort in the group which consists of a nitride of lithium fluoride, a lithium bromide, lithium iodide, a lithium chloride, lithium nitride, a lithium sulfide, a lithium silicate, lithium carbonate, lithium sulfate, Linn-ized lithium, lithium phosphate, and lithium phosphate. Since it was made to contain, the pliability, intensity, or ionic conductivity of an inorganic compound layer can be raised. Especially, since it was made for the nitride of lithium phosphate to be included according to a negative electrode according to claim 6 or the cell according to claim 14, a higher effect can be acquired.

[0090]

Since it was made to make 10 nm of thickness of the inorganic compound layer into less than [super-5micrometer] according to a negative electrode according to claim 7 or the cell according to claim 15, the reaction of an electrolyte and a negative electrode active material layer can be inhibited more, and a higher effect can be acquired.

[Brief Description of the Drawings]

[Drawing 1] It is a sectional view showing the composition of the rechargeable battery concerning a 1st embodiment of this invention.

[Drawing 2] It is an exploded perspective view showing the composition of the rechargeable battery concerning a 2nd embodiment of this invention.

[Drawing 3] It is a sectional view showing the composition which met the III-III line of the electrode winding body shown in drawing 2.

[Description of Notations]

11 [-- Positive active material layer,] -- An armor can, 12, 32 -- An anode, 12A, 31A -- A positive pole collector, 12B, 31B 13 -- An exterior cup, 14, 32 -- A negative electrode, 14A, 32A -- Negative pole collector, 14B, 32B [-- A positive electrode lead 22 / -- A negative electrode lead 30 / -- An electrode winding body 34 / -- An electrolyte layer 35 / -- Masking tape, 40A, 40B / -- An exterior member 41 / -- Adhesion film] -- A negative electrode active material layer, 14C, 32C -- An inorganic compound layer, 15, 33 -- A separator, 21

[Translation done.]